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Influences of heating rate during coal char preparation and AAEMs on volatile–char interaction with different sources of biomass volatile

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ABSTRACT

Volatile–char interaction is important for the operation of co-gasification of coal and biomass. Biomass generally produces large amount of volatiles while char is mainly produced from coal. Hence, in this study, the interaction between coal char and volatiles from biomass samples (xylan, cellulose and rice straw) was examined using a rapid-heating thermobalance reactor. Three types of coal char, consisting of slow pyrolyzed-coal char (Ex-char), fast pyrolyzed-coal char (In-char), and acid washed-coal char (Ac-char), were employed to reveal influences of heating rate during char preparation and retention of alkali and alkaline earth metallic (AAEM) species on char surface. The steam gasification rates of all coal chars in both cases with and without volatile contacting were investigated from the gas evolution rate and remaining char analyses. The results indicate that the steam gasification rates of Ex-char and In-char were significantly diminished by the volatiles derived from all sources, especially rice straw. However, in the case of Ac-char, the reduction of steam gasification rate was less important. Moreover, the Ex-char exhibited the catalyst for the decomposition of biomass volatiles, resulting in the increase in gas production rate. Porous structure and the AAEM over char play crucial roles on the volatile–char interaction.

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1. Introduction

Co-gasification of coal and biomass is a promising way to reduce the environmental impacts of coal and the restrictions of biomass utilization. Recently, a number of co-pyrolysis/gasification studies have been focused on the synergetic effect between coal and biomass in terms of product distribution, gas product composition and the overall process efficiency [1–4]. Volatile–char interaction between coal and biomass is important for ascribing the obvious synergetic effect. For an effective design and operation of co-pyrolysis/gasification, the volatile–char interaction is the one of essential considerations. In the previous studies, the volatile–char interaction on the steam gasification rate of Victorian brown coal has been investigated in a fluidized bed/fixed-bed reactor [5,6] and in a bubbling fluidized bed reactor [7]. The volatiles released from coal pyrolysis as well as coal steam gasification showed the inhibition effect on char steam gasification because of the changing of char structure and char morphology. Furthermore, the reactivity of char has also been measured in a thermogravimetric (TG) analyzer or thermobalance reactor to obtain the real time weight loss of char and further analyze to the reactivity of char [8–10]. However, the effect of volatiles on char reactivity by using the thermobalance reactor is still scarce, especially the operation at high heating rate. Only the present authors who originated and modified the rapid-heating thermobalance reactor (approximately 50 K s^{-1}) into a two-stage reactor (drop tube/thermobalance fixed bed reactor) investigated the effect of volatiles on char reactivity concurrently to examine the effect of char on the volatile decomposition [11]. The authors found that H_2 and the vapor-phase of levoglucosan had an inhibition effect on biomass char steam gasification, resulting in the decrease of reaction rates of char steam gasification and gas evolution [11].

The gasification rate of coal char, especially low-rank coal, has been reported to depend on the condition during coal char preparation, such as heating rate during the coal pyrolysis/carbonization, temperature and holding time as well as the presence of alkali and alkaline earth metallic species (AAEMs) on coal char surface [8,9,12–21]. Char obtained from the carbonization of sub-bituminous coal with a high heating rate exhibited the higher reactivity than those subjected to slow heating rate, corresponding to the increase in surface area [8,9]. The AAEMs on coal char can also catalyze the gasification rate of char through the formation of disordered crystalline of carbon structure [18]. In addition, the catalytic role of char on tar decomposition has been reported [20,22–28]. Hosokai et al. [29,30] studied the catalytic effect of biomass

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char on the decomposition of aromatic compounds. They revealed that the aromatic compounds, which are found in the biomass derived volatiles, can be decomposed over charcoal surface. This was described by the coexisting of coke formation and steam gasification of char. However, the previous investigation has rarely mentioned the gasification rate of coal char, especially prepared from different conditions, in the presence of biomass volatiles. Moreover, less attention has been paid to the influence of heating rate during coal char preparation on the catalytic effect with various sources of biomass volatiles. Therefore, this research was focused on investigating the interaction between coal char and biomass derived volatiles by using a modified rapid-heating thermobalance reactor. Three types of coal char, including slow pyrolyzed-coal char (Ex-char), fast pyrolyzed-coal char (In-char), and acid wasted-coal char (Ac-char), were employed. The effects of surface properties of prepared char as well as the retention of AAEMs on the char surface were discussed in terms of gasification rate of char in contact with various sources of biomass volatiles. The finding in this research is beneficial to an effective design of co-gasification process between coal and biomass.

2. Experimental

2.1. Materials

2.1.1. Coal char

Three types of coal chars were prepared under the different conditions. Ex-char was prepared in a typical fixed bed reactor which was performed elsewhere [31]. Seven grams of Indonesian coal (sub-bituminous coal, particle size: 150–250 μm) was placed inside the quartz reactor (20 mm-ID and 40 cm-heating zone length). The coal was slowly pyrolyzed under the inert N_2 flow rate of 120 $cm^3\ min^{-1}$ as the temperature was increased from 303 to 873 K ~5 $K\ s^{-1}$ and then held at 873 K for 60 min. In-char was prepared inside a thermobalance reactor, schematically shown in Fig. 1, starting with approximately 25 mg sample of Indonesian coal that was placed in the sample holder and then rapidly pyrolyzed at a heating rate of 38 $K\ s^{-1}$ from 388 to 873 K and held at this temperature for 1 min under an Ar atmosphere. This char was immediately subjected to steam gasification testing in the same reactor. Ac-char was prepared in the same way as Ex-char except that the Ex-char was then washed with sulfuric acid solution using a method explained elsewhere [32].

The morphology of the prepared coal chars was characterized by nitrogen adsorption–desorption for Brunauer–Emmett–Teller (BET) analysis (model Quantachrome, Autosorb-1) and by scanning electron microcopy (SEM) (model JEOL, JSM-5410LV) analysis. For BET analysis, samples were at 573 K for 6 h degassed before adsorption. The elemental analysis of coal char was performed by X-ray fluorescence (XRF) (model Philips, PW2400) analysis.

2.1.2. Volatile sources

Three types of volatile sources i.e. cellulose, xylan and rice straw were used in this study. Cellulose (Merk, Co. Ltd.) and xylan from birch wood (Sigma-Aldrich, Co. Ltd.) were sieved to particle size of 75–106 μm. Rice straw, represented the real biomass, was sieved to particle size of 75–180 μm. The rice straw contains with 32% cellulose, 35.7% hemicellulose, 22.3% lignin and 10.0% of the extractive matter [33]. All of samples were dried at 378 K for 12 h and kept in a desiccator before testing. The proximate and ultimate analyses of all volatile sources were also evaluated and the results are summarized in Table 1.

2.2. Steam gasification in a rapid-heating thermobalance reactor

Char steam gasification was carried out in the rapid-heating thermobalance reactor, as illustrated in Fig. 1. The thermobalance reactor consists of quartz 25 mm-ID outer tube, 13 mm-ID inner tube, an infrared gold image furnace and balance sensor (TG-9000HC; ULVAC-RIKO Inc.). A sample holder with platinum mesh filter is suspended with the balance controller. To investigate the effect of volatiles from the different sources on the steam gasification rate of coal char, the thermobalance reactor has been modified as a two-stage reactor (drop tube/thermobalance fixed-bed reactor), in which it was divided to the top and bottom stages by an Inconel® wire mesh filter. The schematic image of the two-stage reactor is shown in Fig. 2. At the top stage, the volatile sources were fed by a departure feeder (Alpha Corporation) with a constant feed rate and

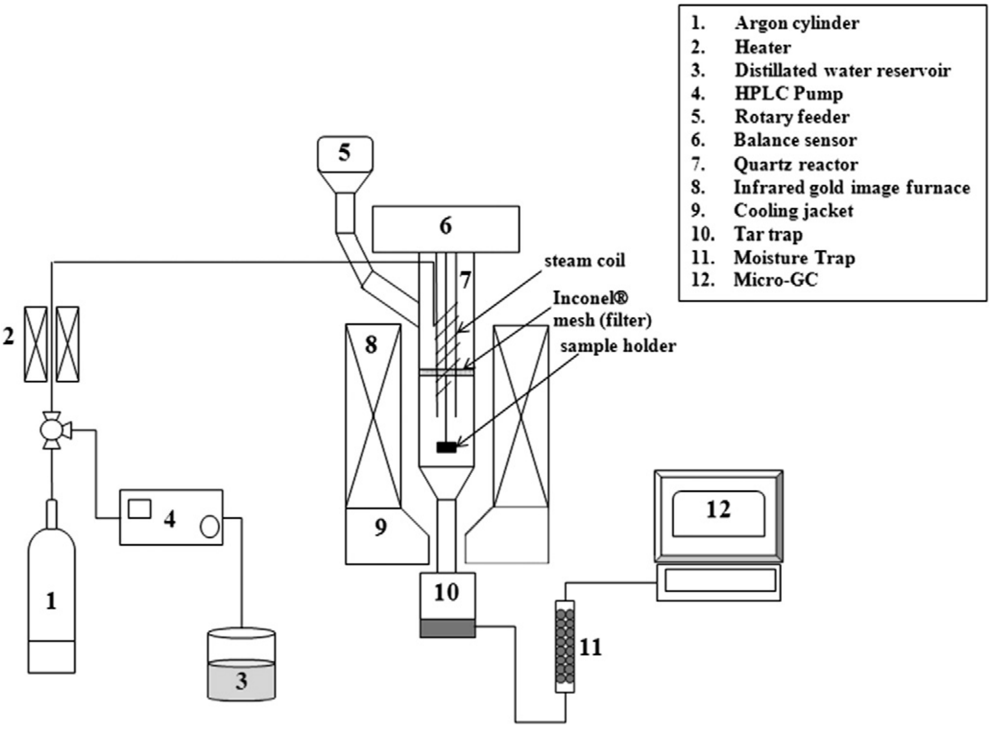

Fig. 1. Schematic image of a thermobalance reactor.

feeding time, which were 12–13 mg min^{-1} for 85 min, 25 mg min^{-1} for 30 min, and 18–19 mg min^{-1} for 30 min for cellulose, xylan and rice straw, respectively. After the temperature reached the set point, the pyrolysis of the volatile sources took place rapidly. Then, the pyrolyzed char of the volatile resource dropped on the filter and only the volatiles passed through to the bottom stage. In the bottom stage, 10 mg of coal char was placed inside the sample holder and so this could make contact with the volatiles that came from the top stage (the "volatile–char contacting zone"). At the same time, steam at 388 K from the steam generator was introduced into the reactor at the bottom stage.

Steam gasification of the char, in contact with the volatiles when provided, took place in the bottom stage of the reactor. The temperature program was performed in two steps. In the first step, it was heated to 388 K with heating rate ~6 K s^{-1} and held at this temperature for 15 min to evaporate any residual water in the sample. In the second step, the sample was heated to 1073 K at a heating rate of 38 K s^{-1}. The weight loss of char in the sample holder was recorded every 0.4 s throughout the 90 min reaction time. Tar and water were condensed in an ice–tar trap and then the non-condensable stream was passed through a moisture capturing plot filling with silica gel. The gas production rate during the steam gasification was analyzed for H_2, N_2, CH_4, CO and CO_2 levels using a thermal conductivity detector-micro gas chromatograph (TCD-micro GC) equipped with MS-5A and Pora Plot Q columns. After steam gasification, the char was burnt by introducing air into the reactor. A blank experiment was performed using exactly the same procedure but with no sample in the ceramic basket so as to compensate the output drift of the thermobalance reactor.

2.3. Data analysis and calculation

In this study, the effect of volatiles on the steam gasification of coal char was investigated in conjunction with the effect of coal char on the decomposition of volatiles. During the steam gasification of char, the overall rate constant (k) of char steam gasification was calculated based on the weight loss of char as expressed in Eq. (1)

$$\frac{dX_{char}}{dt} = -k\frac{1}{1-X_{char}} \tag{1}$$

where X_{char} is the conversion of char during steam gasification. The char conversion was calculated following Eq. (2)

$$X_{char} = \frac{X-X_p}{1-X_p} \tag{2}$$

where X and X_p are the conversion to volatiles at any time (t) and the conversion to volatiles in pyrolysis period, respectively. The steam gasification rate of char was assumed to obey the first-order kinetics. Moreover, the average gas production rate from all volatile sources was calculated and compared between the presence and the absence of coal char sample in the sample holder (at bottom stage).

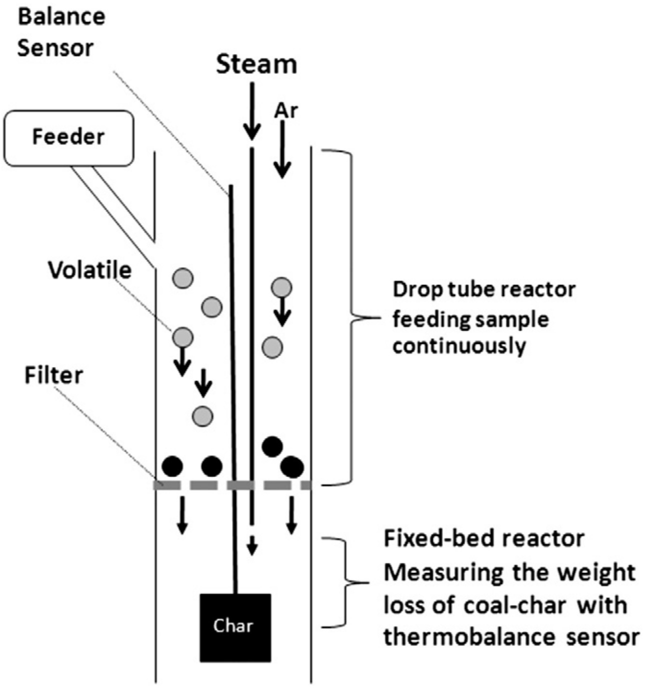
Balance Sensor
Steam
Ar
Feeder
Volatile
Filter
Drop tube reactor feeding sample continuously
Fixed-bed reactor Measuring the weight loss of coal-char with thermobalance sensor
Char

Fig. 2. Schematic of the two-stage reactor (drop tube/thermobalance fixed-bed reactor).

3. Results and discussion

3.1. Steam gasification of coal char without volatile contacting

The time–relative mass profile of the three different prepared coal chars during steam gasification at 1073 K is shown in Fig. 3. Note that the initial time (0 s) was defined as the weight change of the coal char sample during the initial pyrolysis before the temperature reached 1073 K. The result showed that the time–relative mass profiles of all coal chars (Ex-char, In-char and Ac-char) showed similar patterns. The relative mass rapidly decreased in the first stage over the first ~1000 s (~45% for the Ex-char and In-char and 55% for the Ac-char), decreasing in rate to ~4200 s and then decreasing slightly thereafter to the final weight at 5000 s. At 5000 s, the relative mass of the In-char and Ex-char (97% and 93% weight loss) was greater than that of the Ac-char (83%). A summary of final char conversion ($X_{char,final}$) and overall rate constant (k) of the three types of coal char during steam gasification is shown in Table 2. The overall rate constant (k), which implies the reactivity of the coal char, was ordered (highest to lowest) as In-char > Ex-char > Ac-char. In the case of char steam gasification under a rapid heating rate, the catalytic gasification by AAEM species was previously reported to proceed in parallel with non-catalytic steam gasification [7]. In this study reported here, the amount of AAEM species, such as Na, K, Mg and Ca, on the coal char surface was determined by XRF analysis. It revealed that the Ac-char had the lower amount of AAEMs than the Ex-char, especially for Na (15.5-fold) and Ca (11.6-fold) (Table 3).

Table 1
Proximate and ultimate analyses of samples.

Sample	Proximate analysis (wt.%)				Ultimate analysis (wt.% dry ash-free basis)				
	Moisture	Ash	Volatile matter	Fixed carbon	C	H	N	S[a]	O (diff.)
Coal	12.41	8.39	36.84	42.36	72.13	6.67	1.4	0.22	19.58
Rice straw	6.43	11.22	61.95	29.25	45.30	6.93	0.92	0.14	46.71
Cellulose	4.01	0.01	80.30	15.68	35.94	5.82	0.04	n.d.	58.25
Xylan	12.88	8.01	63.95	15.16	37.50	7.15	0.10	n.d.	55.25

n.d. = not determined.
[a] By Bomb washing method (ASTM 3177).

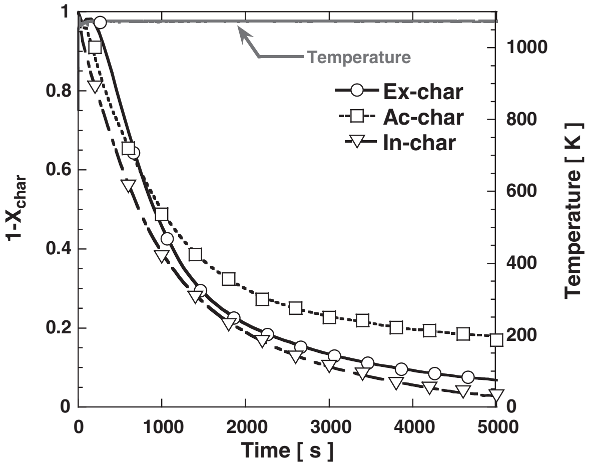

Fig. 3. Time–relative mass profile of the three different prepared coal chars in steam gasification at 1073 K without volatile contacting.

Note that the In-char was not analyzed as insufficient sample was available. It has been reported previously that Na and Ca act as the catalyst in the steam gasification of carbon and coal [34]. Therefore, the loss of AAEM catalytic species, such as the Na and Ca, in the Ac-char caused the reduction in its reactivity. Furthermore, the morphology of Ac-char was drastically changed by the acid washing. BET analysis of the surface area, pore volume and average pore diameter of the Ex-char and Ac-char (In-char was not assayed) revealed that the Ex-char had a larger average BET surface area (9.1-fold) and pore volume (5.2-fold) and a 1.75-fold smaller average pore size than the Ac-char (Table 4). SEM analysis revealed a smooth and/or dense carbon surface for the case of Ac-char compared to that for the Ex-char (Fig. 4). This supports that the structure of the Ac-char was destroyed by acid washing and likely resulted in the decrease in char reactivity. This result agrees with Jamil et al. [35], who revealed that char reactivity was dependent on the catalytic activity of AAEMs and the char surface structure.

On the other hand, the In-char showed the highest reactivity with the largest $X_{char,final}$ of about 0.97 and the overall rate constant (k) of 6.758×10^{-4} s^{-1}, which was more than 52% and 20% higher than the Ac-char and Ex-char, respectively. The higher reactivity of In-char showed a good agreement with the previous studies [8,36,37] which reported the reactivity of biomass char and coal char prepared under a high heating rate. The steam gasification rate of the coal char substantially increased under rapid heating because of the rapid evolution of volatiles which led to the production of a porous char structure [9,16,38]. However, pyrolysis under a high heating rate promoted the volatilization of AAEM species over the char surface and caused the loss of these catalytic species for the char steam gasification [34,39]. The surface structure and the retained AAEMs in case of In-char were not analyzed due to the limitation, as mentioned above. However, it can be expected that the In-char had larger surface area and pore volume but lower amount of the retained AAEMs in comparison with the Ex-char. Therefore, the higher reactivity of the In-char was influenced by the improvement of char surface structure with the minor catalytic effect of AAEM on char surface.

Table 3
Elemental analysis of all volatile resources and all coal chars by XRF technique.

Sample	Element content (wt.%, as received)				
	Na	K	Mg	Ca	Si
Coal char bed					
Ex-char	0.31	0.59	0.41	9.56	10.90
Ac-char	0.02	0.17	0.28	0.82	5.55
In-char	n.d.[a]	n.d.[a]	n.d.[a]	n.d.[a]	n.d.[a]
Volatile resource					
Rice straw	0.06	1.77	0.13	0.69	11.29
Xylan	0.73	0.17	<0.01	2.22	0.05

[a] n.d. = not determined.

3.2. Steam gasification of coal char with volatile contacting

The time–relative mass profile of the three different types of coal char alone or in contact with the all volatiles from cellulose, xylan or rice straw is shown in Fig. 5. The relative mass profile of the Ex-char in contact with the volatiles was dramatically higher than that with the Ex-char alone (Fig. 5a). Thus, the steam gasification rate of the Ex-char was reduced by these volatiles leading to lower $X_{char,final}$ and k values (Table 2). In other words, the volatiles derived from all three volatile sources retarded the reactivity of the Ex-char. However, the volatiles from the different sources differed in their kinetics and magnitude of their induced level of inhibited char steam gasification. The volatiles derived from the rice straw caused the largest inhibition of the Ex-char steam gasification rate, followed by that from xylan with the volatiles derived from cellulose being the least affective. Cellulose is one of the major components in biomass and has been reported as H-donor species during pyrolysis [40]. A number of studies have addressed the inhibition effect of H-donor species on the steam gasification of char [6,7,11,41,42]. Fushimi et al. [11] revealed that the higher hydrogen partial pressure greatly inhibited the gasification rate of biomass char via the reverse oxygen exchange and dissociative hydrogen adsorption reactions as expressed in Eqs. (3) and (4).

$$\text{Reverse oxygen exchange}: \quad C(O) + H_2 \leftrightarrow C + H_2O \tag{3}$$

$$\text{Dissociative hydrogen adsorption}: \quad C + {}^{1}\!/_{2}H_2 \leftrightarrow C(H) \tag{4}$$

Table 2
The final char conversion ($X_{char,final}$) and the overall rate constant (k) of char steam gasification at 1073 K.

Coal char	Volatile resources	Char conversion at t = 5000 s ($X_{char,final}$)	Overall rate constant, ($k \times 10^4$ s^{-1})	Regression coefficient (R^2)
Ex-char	–	0.932	5.44	0.95
Ex-char	Cellulose	0.883	4.14	0.94
Ex-char	Xylan	0.894	4.63	0.99
Ex-char	Rice straw	0.863	4.05	0.99
In-char	–	0.972	6.76	0.99
In-char	Cellulose	0.866	3.62	0.91
In-char	Xylan	0.910	4.94	0.98
In-char	Rice straw	0.707	2.44	0.97
Ac-char	–	0.831	3.22	0.89
Ac-char	Cellulose	0.865	4.37	0.97
Ac-char	Xylan	0.730	2.50	0.90
Ac-char	Rice straw	0.842	3.99	0.99

Table 4
BET surface area, pore volume and average pore size of coal char.

Coal char sample	Ex-char	Ac-char
BET surface area ($m^2\ g^{-1}$)	200.71	21.99
Pore volume ($cm^3\ g^{-1}$)	0.1389	0.0266
Average pore size (A°)	27.68	48.33

Bayarsaikhan et al. [7] also reported that the non-catalytic char steam gasification was greatly decelerated by the presence of H_2 due to its dissociative chemisorption onto free carbon (C) sites forming H-laden carbon (C(H)). However, the level of retardation by H_2 was not strong enough to inhibit the steam gasification of char, unlike the H-radical from volatiles [7]. The dissociative chemisorption of hydrogen radical from the thermal cracking of volatiles in the gas phase, as in Eq. (5), prevented the progress of char steam gasification.

$$\text{Dissociative H-radical from volatile chemisorption:} \quad C + H \leftrightarrow C(H) \tag{5}$$

For the In-char, all three volatile sources also inhibited the char steam gasification rate (Fig. 5b), with the $X_{char,final}$ and k values (highest to lowest) as In-char > xylan + In-char > cellulose + In-char > rice straw + In-char (Table 2). The inhibition effect on the In-char reactivity showed the same trend as with the Ex-char (Fig. 5a), but the reduction of the steam gasification rate of the In-char by volatile contacting was more significant. Presumably the heating rate and holding time during char preparation are important factors that influence the char structure and its reactivity. The rapid release of volatiles under high heating rate pyrolysis caused the formation of highly porous char which is mostly mesopores and macropores. These mesopores and macropores have been reported to act as the active sites for char gasification [10,16,38,43] and the inductive sites for coke formation from the large molecular weight hydrocarbons [44]. Moreover, in the presence of volatiles, the competition between char steam gasification and carbon deposition by volatiles occurred [7]. The coke formation might be more dominant than coke steam gasification in case of the In-char, leading to the high solid residues, as can be seen in Table 2. Another reason was the promotion of AAEM volatilization on coal char such as Na, K and Ca (Eq. (6)) in the presence of volatiles, resulting in the loss of catalytic species for steam gasification of char [45].

$$\text{Volatilization of AAEM by R radical:} \quad R + CM{-}X \leftrightarrow CM{-}R + X \tag{6}$$

where R, CM and X represent the free radical from volatiles (mainly H-radical), char matrix and AAEM species, respectively. Considering the type of volatile sources, the volatiles derived from rice straw showed the strongest inhibition of the In-char reactivity compared to those from cellulose or xylan. The effect of volatile sources will be discussed accompanying with the result of gas production in the next section.

With respect to the Ac-char, the three types of volatiles showed broadly similar inhibition patterns (Fig. 5c.) but with the final char conversion ($X_{char,final}$) and k values all being close to ~0.8 and $4 \times 10^{-4}\ s^{-1}$, respectively (Table 2). Thus, the volatiles derived from cellulose as well as rice straw gave no significant effect on the steam gasification rate of the Ac-char. It was relevant to the lower porosity and the lower amount of the retained AAEMs on the Ac-char surface. However, the contacting with the volatiles from xylan induced a slightly lower $X_{char,final}$ and k values than the volatiles derived from other two sources. The notable inhibition of xylan on the Ac-char was attributed to a possibility of forming non-reactive carbon (coke) over the Ac-char.

3.3. Decomposition of the volatile sources with and without coal char

During the steam gasification of coal char in the presence of the volatiles, volatile decomposition took place simultaneously with the char steam gasification within the same reactor. The average gas production rate derived from the decomposition of cellulose, xylan and rice straw volatiles, with and without coal char during steam gasification at 1073 K is summarized in Fig. 6. Note that the data represents the net gas production rate obtained from the volatile sources excluding the gas evolution from the coal char. In the absence of coal chars, cellulose preferentially decomposed to produce CO and H_2 as the main gaseous products while CH_4 and CO_2 were minor components (Fig. 6a). In contrast, a significantly lower total gas production level was attained with xylan than with cellulose and the proportion of CO and CH_4 was much lower, while that of CO_2 and H_2 was much higher (Fig. 6b). This result was consistent with the previous studies [46,47], which reported that in the pyrolysis and in air-steam gasification of cellulose and xylan, the main gaseous products were H_2, CO and CO_2 with cellulose providing a higher CO production level than xylan, while xylan gave a higher amount of CO_2 production. Cellulose has a high ether (C–O–C) and carbonyl (C═O) content that can potentially promote CO production, whereas CO_2 is mainly produced from hemicellulose (mainly xylan) due to the cracking and reforming of the ketone (C═O) and carboxyl (COOH) groups [48]. The total gas production from rice straw was almost the same as that from xylan, but showed a relatively higher production level and percentage proportion of CH_4 and CO and a lower H_2 level (Fig. 6c). This is likely to reflect the higher amount of lignin in the starting rice straw (~22 wt.%) [47].

The effect of the three different coal chars on the cellulose decomposition, in terms of the H_2, CH_4, CO and CO_2 gas production, is shown in Fig. 6a. It revealed that the presence of Ex-char increased the total gas production level. Consider gas composition, the presence of Ex-char provided the higher in H_2 and CO production than that pure cellulose. It indicates that the Ex-char acted as a catalyst for cellulose derived tar steam reforming (Eq. (7)).

$$\text{Tar steam reforming:} \quad C_nH_m + nH_2O \leftrightarrow nCO + (n + {}^{m}/_{2})H_2 \tag{7}$$

The catalytic effect of char, which is derived from the pyrolysis of biomass and the low rank coal, on the decomposition of volatiles has

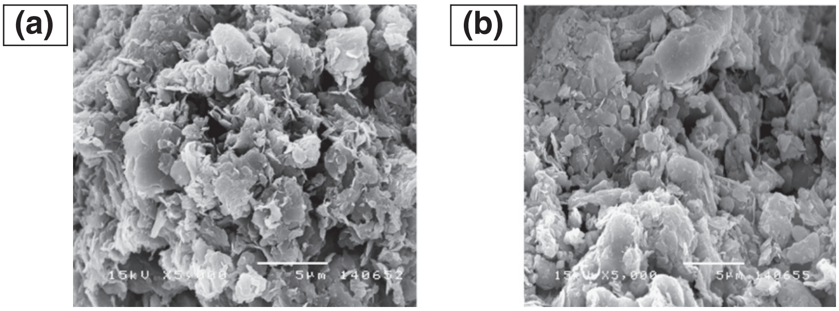

Fig. 4. SEM images of (a) Ex-char and (b) Ac-char.

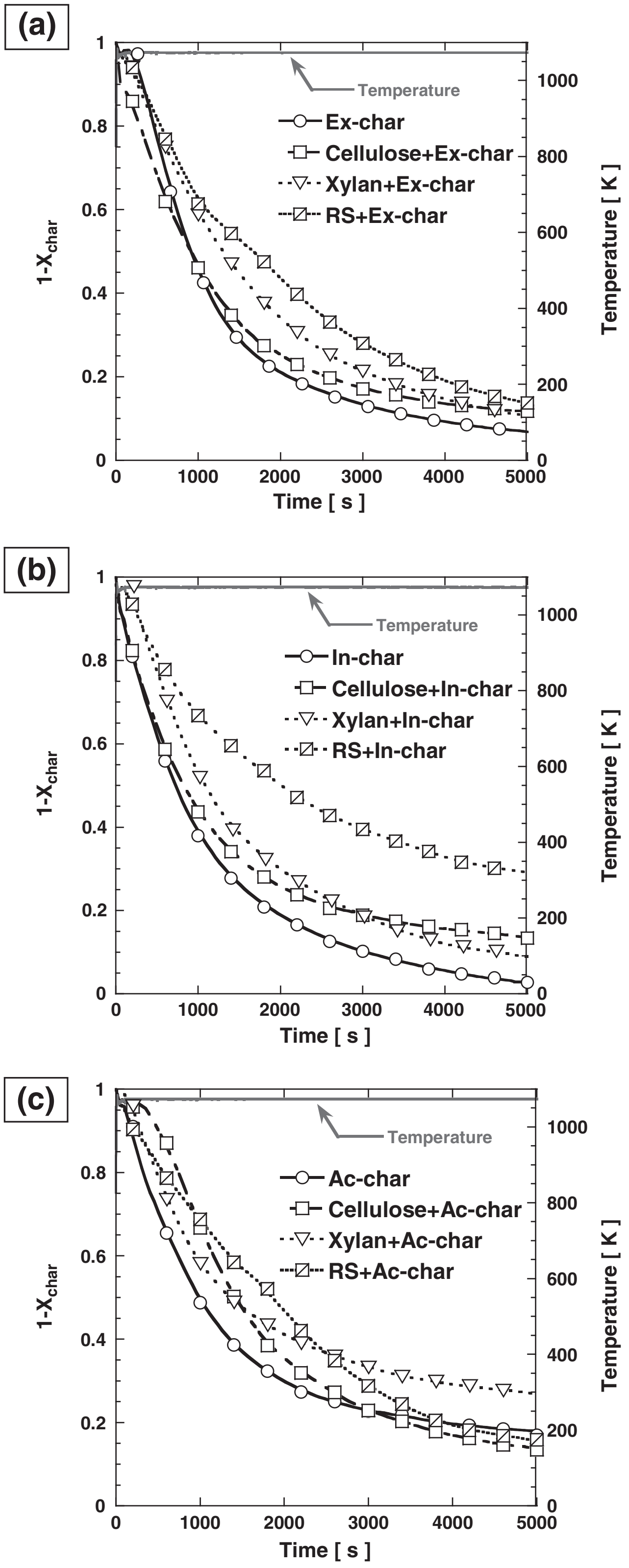

Fig. 5. Time–relative mass profile of the three different prepared coal chars in steam gasification at 1073 K with volatile contacting (a) Ex-char, (b) In-char and (c) Ac-char.

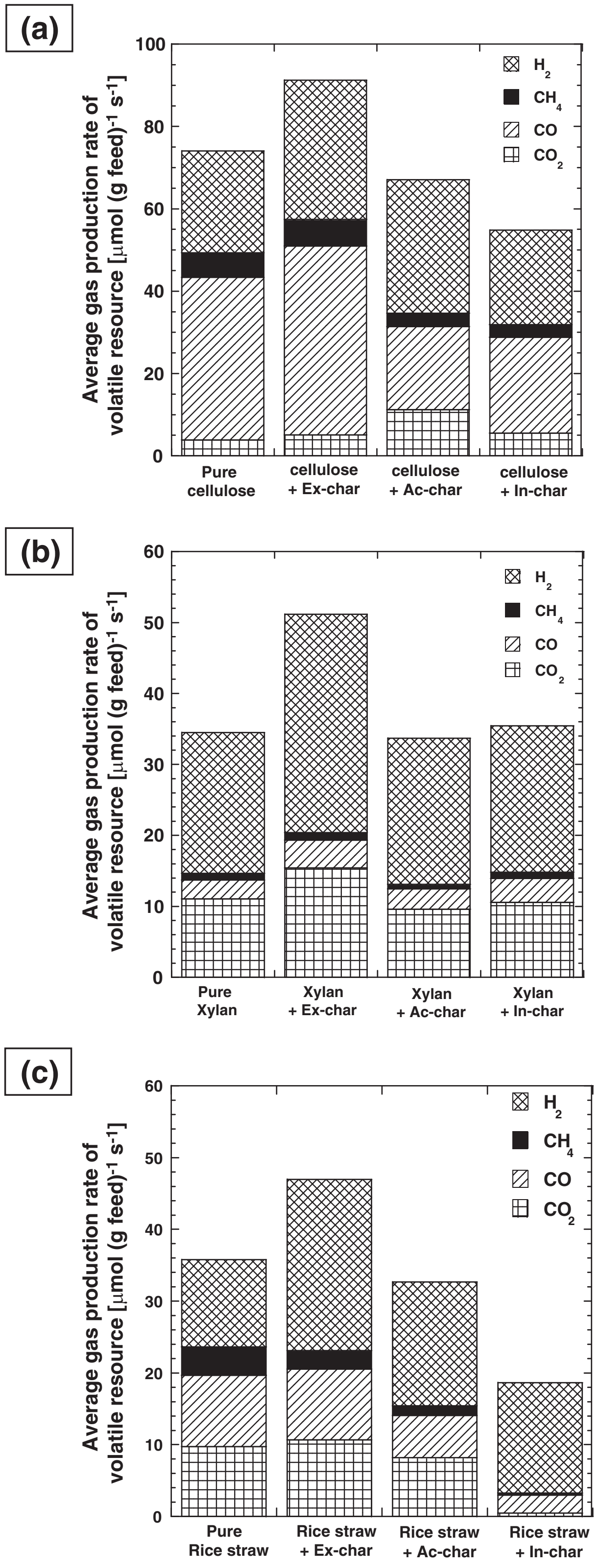

Fig. 6. Average gas production rate derived from the decomposition of cellulose, xylan and rice straw volatiles, with and without coal char during steam gasification at 1073 K (a) cellulose, (b) xylan and (c) rice straw.

been evaluated in several studies [22,28,29,49,50]. It was previously reported that the decomposition of nascent volatiles, especially aromatic compounds, over the char surface underwent following two mechanistic steps i.e. the deposition of nascent tars over the char surface to form coke followed by the steam gasification of char/coke to generate the gaseous products [29,30]. The rate of both reaction steps was relied on the porosity of the char (surface area, pore volume and pore size) and the presence of catalytic AAEM species, such as Na, K and Ca on the

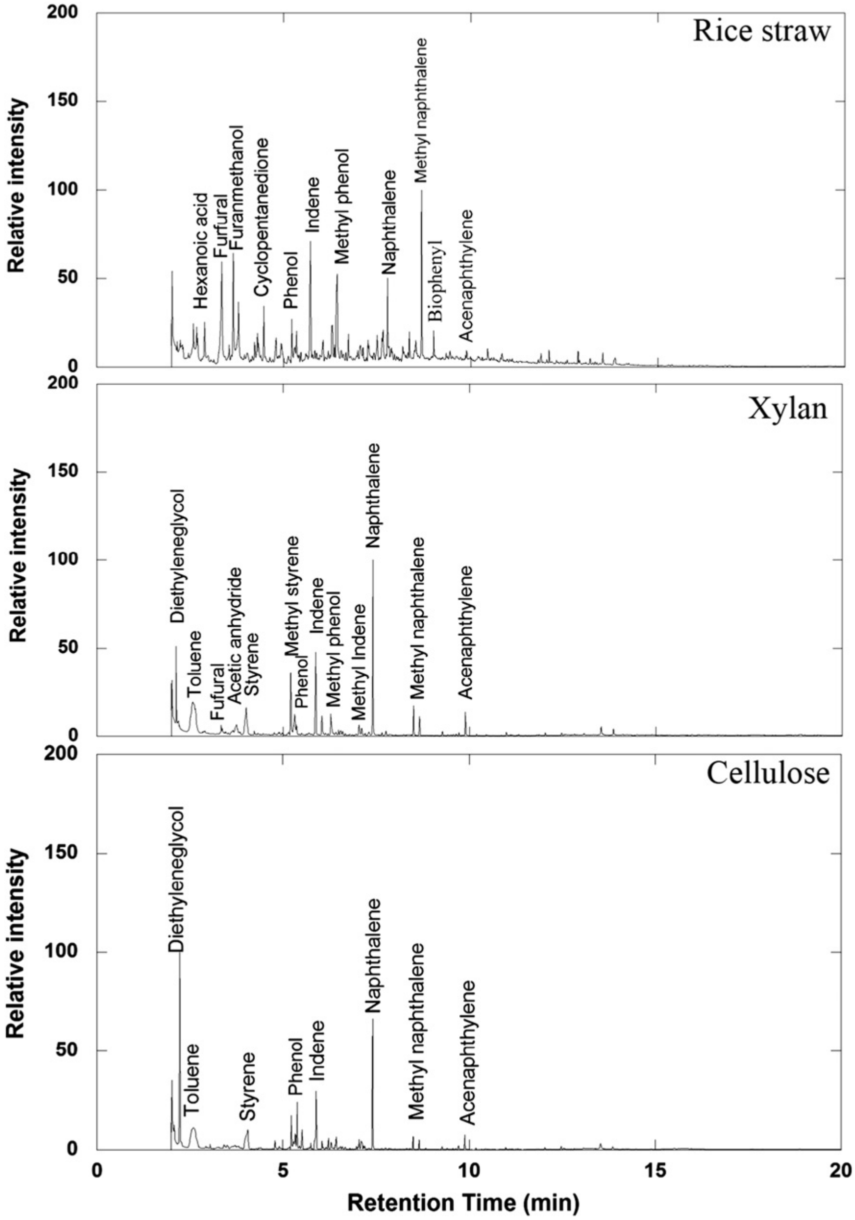

Fig. 7. GC/MS pattern of the volatiles derived from the pyrolysis of rice straw, xylan and cellulose.

char surface [29,30]. In this study, the catalytic effect of the Ex-char was observed due to its large surface area (200.7 $m^2\ g^{-1}$) (Table 4) and high level of inherent AAEM, especially the Ca content (Table 3). Na- and Ca-remaining in coal char were reported as the active catalyst for the nascent tar/soot decomposition [50] as well as carbon steam gasification [34].

Conversely, the presence of Ac-char and In-char provided a lower total gas production level than with the Ex-char, and was even lower than that produced by cellulose alone. This result indicates that the catalytic role of the Ac-char and In-char on tar reduction was not found but the hindrance of tar reduction was observed instead. Even though the Ac-char structure was not preferable to form coke alike the Ex-char, the gas composition results, the higher H_2 and lower CH_4 production, showed that the possible coking occurs in this experimental system. The coke formation from methane and hydrocarbons underwent following Eqs. (8) and (9).

$$\text{Coking from methane}: \quad CH_4 \rightarrow C + 2H_2 \tag{8}$$

$$\text{Coking from hydrocarbon}: \quad C_nH_{2n+2} \leftrightarrow nC + (n+1)H_2 \tag{9}$$

As mentioned above, the subsequence steam gasification of coke would be progressed and generated the gas products. In this case, the rate of coke steam gasification was slower than coking due to the loss of AAEM species over char surface that led to produce low content of gaseous product. Similarly with the case of In-char, the promotion of the volatilization of AAEMs by volatiles resulted to reduce the rate of coke steam gasification, while the active structure of the In-char induced to form more coke over its surface. Therefore, the total gas production in case of the In-char was lower than that in case of Ac-char.

Considering the effect of coal char on xylan and rice straw decomposition (Fig. 6b and c), it was found that the presence of Ex-char gave the higher total gas production than the absence of coal char and provided the higher in H_2, CO and CO_2 production. It indicates that the Ex-char acts as the catalyst for steam reforming of tar derived from rice straw and also coke steam gasification because of its active surface as mentioned above. In addition, it can be noticed that the Ex-char plays a

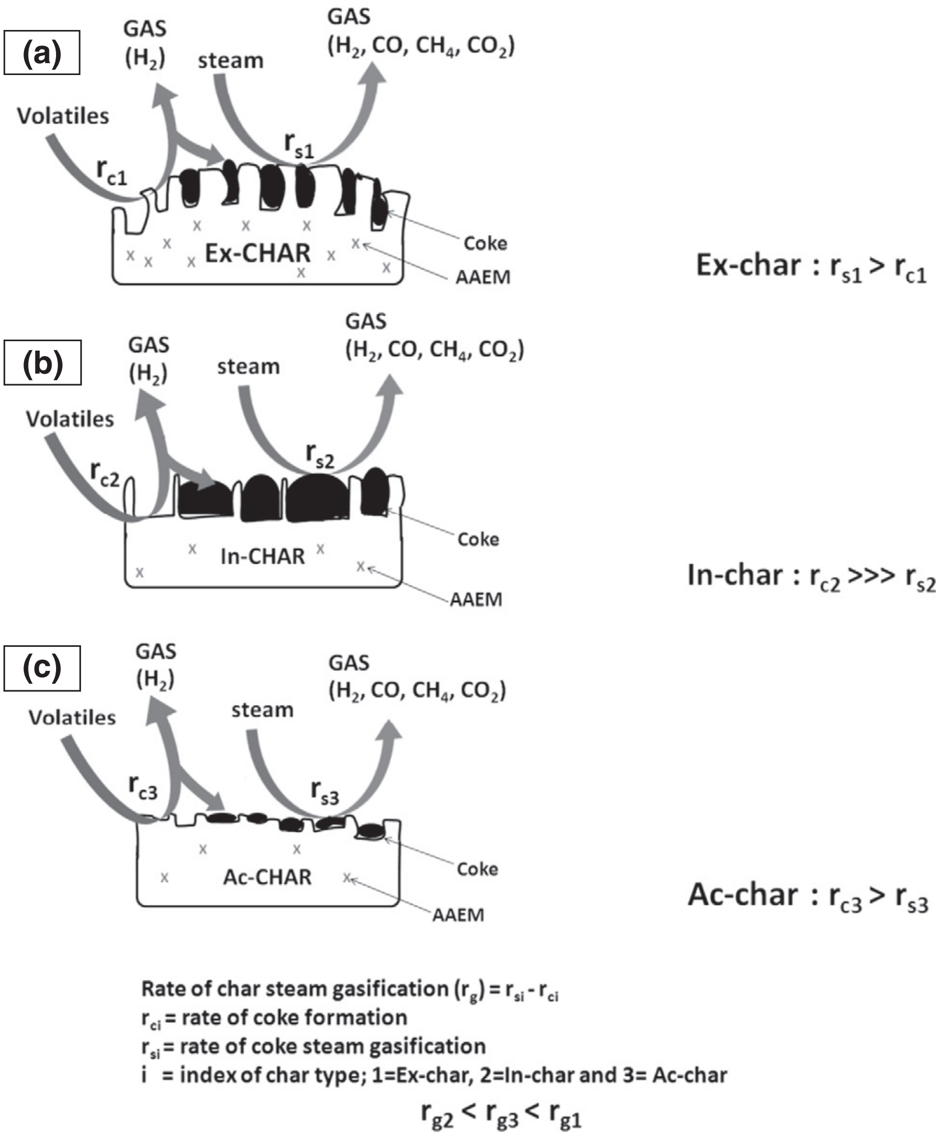

Fig. 8. Interaction between the volatiles and three types of prepared coal char (a) Ex-char, (b) In-char and (c) Ac-char.

catalytic role on the decomposition of CH_4 resulting in the essential decrease of CH_4, as can be seen in Fig. 6c. This result was consistent with the study by Bai et al. [51] who stated that coal char could be a catalyst for methane decomposition. They revealed that the catalytic methane decomposition over coal char mainly occurred within its micropores and the mineral in its ash had a little effect [51]. The effect of Ac-char and In-char on gas evolution of xylan and rice straw showed the similar results with the case of cellulose (Fig. 6a). However, it was noticeable that the gas evolution from rice straw with the presence of In-char had the lowest content among all experiments. It could be stated that the secondary reaction such as soot and coke formation in the case of rice straw derived volatiles with the presence of In-char was more significant than steam gasification of the formed coke. This result shows a good agreement with the reactivity of the In-char, as mentioned in Section 3.2. Condensable volatiles, so-called tar, released during the pyrolysis of different sources were characterized by GC–MS analysis, the result is shown in Fig. 7. It was found that the volatiles derived from rice straw were mainly comprised of aromatic compounds, such as phenol, naphthalene and anthracene which trended to form coke/soot over char surfaces easier than the saccharide units, such as furfural in the volatiles derived from cellulose and xylan. Coke formation from the heavy tar or polyaromatic hydrocarbons (PAHs), via ring condensation and crosslink reaction, was more extensive on the carbonaceous material as well as the porous alumina [22]. On the other hand, the coke from the aromatics or high molecular weight hydrocarbon is hardly decomposed by steam. Interaction between volatiles and three types of coal char depended on the rate of competitive reactions between coke formation (r_{ci}) and coke steam gasification (r_{si}), as summarized in Fig. 8. Finally, the steam gasification rate of coal char (r_g) with volatile contacting can be ordered as Ex-char > Ac-char > In-char.

4. Conclusions

In this study, the interaction between coal char, prepared by three different conditions, and volatiles from cellulose, xylan and rice straw was examined in a rapid-heating thermobalance reactor. Analysis of the effect of the different volatile sources on the various types of coal char was carried out concurrently with analysis of the effect of coal char on the decomposition of volatiles. In summary, four main conclusions can be drawn. Firstly, the reactivity of char in steam gasification without volatile contacting was dependent upon char preparation condition and was ranked (highest to lowest) as In-char > Ex-char > Ac-char. This order is likely to be explained by the differences in their structures and the levels of inherent AAEM catalytic species. Secondly, the volatiles derived from all sources caused inhibition of the steam gasification rate of the Ex-char as well as the In-char. On the other hand, the lower porosity and the lower amount of the retained AAEMs on the Ac-char surface showed no significant inhibition of its otherwise low char reactivity. Thirdly, the volatiles derived from rice straw seem to significantly hinder the steam gasification rate of coal char more than the volatiles derived from cellulose and xylan. Lastly, the Ex-char showed a strong catalytic effect on tar decomposition resulting in an increased H_2, CO and CO_2 evolution rates. The catalytic effect was not observed in the presence of the Ac-char or In-char but rather secondary reactions such as coke formation, were dominant instead. The benefit of this study is expected to be the potential advancement in the design of the co-gasification process between coal and biomass.

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References

[1] L. Zhang, S.P. Xu, W. Zhao, S.Q. Liu, Co-pyrolysis of biomass and coal in a free fall reactor, Fuel 86 (2007) 353–359.
[2] T. Sonobe, N. Worasuwannarak, S. Pipatmanomai, Synergies in co-pyrolysis of Thai lignite and corncob, Fuel Processing Technology 89 (2008) 1371–1378.
[3] K. Kumabe, T. Hanaoka, S. Fujimoto, T. Minowa, K. Sakanishi, Co-gasification of woody biomass and coal with air and steam, Fuel 86 (2007) 684–689.
[4] C.A. Alzate, F. Chejne, C.F. Valdes, A. Berrio, J. De La Cruz, C.A. Londono, CO-gasification of pelletized wood residues, Fuel 88 (2009) 437–445.
[5] S. Zhang, Z. Min, H.-L. Tay, M. Asadullah, C.-Z. Li, Effects of volatile–char interactions on the evolution of char structure during the gasification of Victorian brown coal in steam, Fuel 90 (2011) 1529–1535.
[6] S. Zhang, J.-i. Hayashi, C.-Z. Li, Volatilisation and catalytic effects of alkali and alkaline earth metallic species during the pyrolysis and gasification of Victorian brown coal. Part IX. Effects of volatile–char interactions on char–H_2O and char–O_2 reactivities, Fuel 90 (2011) 1655–1661.
[7] B. Bayarsaikhan, N. Sonoyama, S. Hosokai, T. Shimada, J.-i. Hayashi, C.-Z. Li, T. Chiba, Inhibition of steam gasification of char by volatiles in a fluidized bed under continuous feeding of a brown coal, Fuel 85 (2006) 340–349.
[8] A. Marcilla, M. Asensio, I. Martín-Gullón, Influence of the carbonization heating rate on the physical properties of activated carbons from a sub-bituminous coal, Carbon 34 (1996) 449–456.
[9] H.Y. Cai, A.J. Güell, I.N. Chatzakis, J.Y. Lim, D.R. Dugwell, R. Kandiyoti, Combustion reactivity and morphological change in coal chars: effect of pyrolysis temperature, heating rate and pressure, Fuel 75 (1996) 15–24.
[10] X. Wang, R. He, Y. Chen, Evolution of porous fractal properties during coal devolatilization, Fuel 87 (2008) 878–884.
[11] C. Fushimi, T. Wada, A. Tsutsumi, Inhibition of steam gasification of biomass char by hydrogen and tar, Biomass Bioenergy 35 (2011) 179–185.
[12] K. Hashimoto, K. Miura, T. Ueda, Correlation of gasification rates of various coals measured by a rapid heating method in a steam atmosphere at relatively low temperatures, Fuel 65 (1986) 1516–1523.
[13] K. Miura, K. Hashimoto, P.L. Silveston, Factors affecting the reactivity of coal chars during gasification, and indices representing reactivity, Fuel 68 (1989) 1461–1475.
[14] S. Wu, J. Gu, L. Li, Y. Wu, J. Gao, The reactivity and kinetics of Yanzhou coal chars from elevated pyrolysis temperatures during gasification in steam at 900–1200 °C, Process Safety and Environmental Protection 84 (2006) 420–428.
[15] L. Lu, C. Kong, V. Sahajwalla, D. Harris, Char structural ordering during pyrolysis and combustion and its influence on char reactivity, Fuel 81 (2002) 1215–1225.
[16] C. Fushimi, K. Araki, Y. Yamaguchi, A. Tsutsumi, Effect of heating rate on steam gasification of biomass. 1. Reactivity of char, Industrial and Engineering Chemistry Research 42 (2003) 3922–3928.
[17] R. Gadiou, Y. Bouzidi, G. Prado, The devolatilisation of millimetre sized coal particles at high heating rate: the influence of pressure on the structure and reactivity of the char, Fuel 81 (2002) 2121–2130.
[18] X. Shenqi, Z. Zhijie, X. Jie, Y. Guangsuo, W. Fuchen, Effects of alkaline metal on coal gasification at pyrolysis and gasification phases, Fuel 90 (2011) 1723–1730.
[19] C.Z. Li, Some recent advances in the understanding of the pyrolysis and gasification behaviour of Victorian brown coal, Fuel 86 (2007) 1664–1683.
[20] L.X. Zhang, S. Kudo, N. Tsubouchi, J.-i. Hayashi, Y. Ohtsuka, K. Norinaga, Catalytic effects of Na and Ca from inexpensive materials on in-situ steam gasification of char from rapid pyrolysis of low rank coal in a drop-tube reactor, Fuel Processing Technology 113 (2013) 1–7.
[21] J. Bai, W. Li, C.-z. Li, Z.-q. Bai, B.-q. Li, Influences of mineral matter on high temperature gasification of coal char, Journal of Fuel Chemistry and Technology 37 (2009) 134–138.
[22] S. Hosokai, J.I. Hayashi, T. Shimada, Y. Kobayashi, K. Kuramoto, C.Z. Li, T. Chiba, Spontaneous generation of tar decomposition promoter in a biomass steam reformer, Chemical Engineering Research and Design 83 (2005) 1093–1102.
[23] Z. Min, P. Yimsiri, M. Asadullah, S. Zhang, C.-Z. Li, Catalytic reforming of tar during gasification. Part II. Char as a catalyst or as a catalyst support for tar reforming, Fuel 90 (2011) 2545–2552.
[24] A. Nzihou, B. Stanmore, P. Sharrock, A review of catalysts for the gasification of biomass char, with some reference to coal, Energy 58 (2013) 305–317.
[25] L.X. Zhang, T. Matsuhara, S. Kudo, J.I. Hayashi, K. Norinaga, Rapid pyrolysis of brown coal in a drop-tube reactor with co-feeding of char as a promoter of in situ tar reforming, Fuel 112 (2013) 681–686.
[26] Z. Min, J.Y. Lin, P. Yimsiri, M. Asadullah, C.Z. Li, Catalytic reforming of tar during gasification. Part V. Decomposition of NOx precursors on the char-supported iron catalyst, Fuel 116 (2014) 19–24.
[27] Z. Abu El-Rub, E.A. Bramer, G. Brem, Experimental comparison of biomass chars with other catalysts for tar reduction, Fuel 87 (2008) 2243–2252.
[28] Q. Sun, S. Yu, F. Wang, J. Wang, Decomposition and gasification of pyrolysis volatiles from pine wood through a bed of hot char, Fuel 90 (2011) 1041–1048.
[29] S. Hosokai, K. Kumabe, M. Ohshita, K. Norinaga, C.Z. Li, J.I. Hayashi, Mechanism of decomposition of aromatics over charcoal and necessary condition for maintaining its activity, Fuel 87 (2008) 2914–2922.
[30] S. Hosokai, K. Norinaga, T. Kimura, M. Nakano, C.-Z. Li, J.-i. Hayashi, Reforming of volatiles from the biomass pyrolysis over charcoal in a sequence of coke deposition and steam gasification of coke, Energy & Fuels 25 (2011) 5387–5393.
[31] S. Krerkkaiwan, C. Fushimi, A. Tsutsumi, P. Kuchonthara, Synergetic effect during co-pyrolysis/gasification of biomass and sub-bituminous coal, Fuel Processing Technology 115 (2013) 11–18.
[32] C. Sathe, Y.Y. Pang, C.Z. Li, Effects of heating rate and ion-exchangeable cations on the pyrolysis yields from a Victorian brown coal, Energy & Fuels 13 (1999) 748–755.
[33] J. Wannapeera, B. Fungtammasan, N. Worasuwannarak, Effects of temperature and holding time during torrefaction on the pyrolysis behaviors of woody biomass, Journal of Analytical and Applied Pyrolysis 92 (2011) 99–105.
[34] J.I. Hayashi, M. Iwatsuki, K. Morishita, A. Tsutsumi, C.Z. Li, T. Chiba, Roles of inherent metallic species in secondary reactions of tar and char during rapid pyrolysis of brown coals in a drop-tube reactor, Fuel 81 (2002) 1977–1987.
[35] K. Jamil, C.Z. Li, Volatilisation and catalytic effects of AAEM species on reactivity of char from pyrolysis and gasification of Victorian brown coal, Journal of Energy and Environment 5 (2006) 31–44.
[36] E. Cetin, R. Gupta, B. Moghtaderi, Effect of pyrolysis pressure and heating rate on radiata pine char structure and apparent gasification reactivity, Fuel 84 (2005) 1328–1334.
[37] R. Zanzi, K. Sjostrom, E. Bjornbom, Rapid high-temperature pyrolysis of biomass in a free-fall reactor, Fuel 75 (1996) 545–550.
[38] O. Onay, Influence of pyrolysis temperature and heating rate on the production of bio-oil and char from safflower seed by pyrolysis, using a well-swept fixed-bed reactor, Fuel Processing Technology 88 (2007) 523–531.
[39] T. Okuno, N. Sonoyama, J. Hayashi, C.Z. Li, C. Sathe, T. Chiba, Primary release of alkali and alkaline earth metallic species during the pyrolysis of pulverized biomass, Energy & Fuels 19 (2005) 2164–2171.
[40] T. Hosoya, H. Kawamoto, S. Saka, Solid/liquid- and vapor-phase interactions between cellulose- and lignin-derived pyrolysis products, Journal of Analytical and Applied Pyrolysis 85 (2009) 237–246.
[41] D.M. Keown, J.I. Hayashi, C.Z. Li, Effects of volatile–char interactions on the volatilisation of alkali and alkaline earth metallic species during the pyrolysis of biomass, Fuel 87 (2008) 1187–1194.
[42] X.J. Li, H.W. Wu, J.I. Hayashi, C.Z. Li, Volatilisation and catalytic effects of alkali and alkaline earth metallic species during the pyrolysis and gasification of Victorian brown coal. Part VI. Further investigation into the effects of volatile–char interactions, Fuel 83 (2004) 1273–1279.
[43] F. Mermoud, S. Salvador, L. Van de Steene, F. Golfier, Influence of the pyrolysis heating rate on the steam gasification rate of large wood char particles, Fuel 85 (2006) 1473–1482.
[44] S.D. Carter, D.N. Taulbee, T.L. Robl, The relative coke-inducing tendencies of pyrolysed, gasified and combusted Devonian oil shales, Fuel 72 (1993) 851–854.
[45] H. Wu, D.M. Quyn, C.-Z. Li, Volatilisation and catalytic effects of alkali and alkaline earth metallic species during the pyrolysis and gasification of Victorian brown coal. Part III. The importance of the interactions between volatiles and char at high temperature, Fuel 81 (2002) 1033–1039.
[46] T. Hanaoka, S. Inoue, S. Uno, T. Ogi, T. Minowa, Effect of woody biomass components on air-steam gasification, Biomass and Bioenergy 28 (2005) 69–76.
[47] C. Wu, Z. Wang, J. Huang, P.T. Williams, Pyrolysis/gasification of cellulose, hemicellulose and lignin for hydrogen production in the presence of various nickel-based catalysts, Fuel 106 (2013) 697–706.
[48] H.P. Yang, R. Yan, H.P. Chen, D.H. Lee, C.G. Zheng, Characteristics of hemicellulose, cellulose and lignin pyrolysis, Fuel 86 (2007) 1781–1788.
[49] P. Gilbert, C. Ryu, V. Sharifi, J. Swithenbank, Tar reduction in pyrolysis vapours from biomass over a hot char bed, Bioresource Technology 100 (2009) 6045–6051.
[50] O. Masek, N. Sonoyama, E. Ohtsubo, S. Hosokai, C.Z. Li, T. Chiba, J. Hayashi, Examination of catalytic roles of inherent metallic species in steam reforming of nascent volatiles from the rapid pyrolysis of a brown coal, Fuel Processing Technology 88 (2007) 179–185.
[51] Z. Bai, H. Chen, W. Li, B. Li, Hydrogen production by methane decomposition over coal char, International Journal of Hydrogen Energy 31 (2006) 899–905.